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Bengal gram seed husk as an adsorbent for the removal of dyes from aqueous solutions – Column studies

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Abstract A continuous fixed bed (column) study was carried out by using seed husk of Bengal gram (*Cicer arietinum*) (SHBG) as a biosorbent for the removal of direct dye, Congo red (CR) from aqueous solutions. The effects of important factors, such as the value of initial pH, the flow rate, the influent concentration of CR, bed depth, particle size of SHBG, foreign ions and regeneration of CR were studied. The effect of similar type of direct dyes like direct turquoise blue 86 (DTB) and direct black 38 (DB) on the adsorption of CR in column containing SHBG is also studied by keeping other parameters constant. The studies confirmed that the breakthrough curves were dependent on flow rate, initial dye concentration, size of SHBG, initial pH of solution of CR and bed depth. The bed depth service time analysis (BDST) model was applied at different bed depths to predict the breakthrough curves. The model is found suitable for describing the biosorption process of the dynamic behaviour of the SHBG column and the data were in good agreement with BDST model. When the flow rate was 0.67 mL/min and the influent concentration of CR was mg L^{-1}, the column capacity was 6.572 mg g^{-1}. The removal capacity of SHBG was more in case of CR (6.572 mg g^{-1}) compared to other similar direct dyes of DTB (1.984 mg g^{-1}) and DB (1.612 mg g^{-1}). The removal of CR was enhanced in the presence of foreign ion potassium (8.308 mg g^{-1}) and decreased in the presence of calcium (5.58 mg g^{-1}). 120 ml of acetone is required for the completion of regeneration of the column and the total amount of CR recovered in this case. All the results suggested SHBG as a potential adsorbent for removal of CR from aqueous solution so that the rate of bio-sorption process is rapid.

1. Introduction

The worldwide high level of dye production and their extensive use in many applications generate coloured wastewaters which cause severe water pollution. The coloured dye effluents are generally considered to be highly toxic to the aquatic biota (Walsh and Bahner, 1980). Many health related problems such

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as allergy, dermatitis, skin irritation, cancer, and mutations in humans are associated with dye pollution in water (Ray, 1986; Bhattacharyya and Sharma, 2004). Thus, the removal of dyes from effluents before they are mixed up with natural water bodies is important. Therefore, treatment of dye house wastewater before letting the industrial effluents into the water streams is necessary. So many conventional methods like biological treatment, coagulation, membrane process, ion exchange etc. are available for the treatment of coloured industrial wastewaters. But, these methods suffer with so many drawbacks. Therefore, searching alternate non-conventional methods is required. Research is being done in this direction. Some non-conventional low cost materials like citrus waste (Asgher and Bhatti, 2012), mango leaves (Murugan et al., 2010), banana peel (Amela et al., 2012), tannins (Sanchez-Martin et al., 2011), cellulose fibres (Alila and Boufi, 2009), peanut hull (Zhong et al., 2012), sugarcane bagasse (Zhang et al., 2013), spent brewery grains (Jaikumar et al., 2009), bokbunja seed waste (Binupriya et al., 2009), natural dye waste (Vankar et al., in press), coffee grounds (Hirata et al., 2002), hen feathers (Gupta et al., 2006; Mittal 2006), rice straw (Gonga et al., 2008), rice husk (Lakshmi et al., 2009), jackfruit leaf powder (Tamez Uddin et al., 2009), ginger waste (Ahmad and Kumar, 2010), bamboo culms (Wang 2012), silkworm pupa (Noroozi et al., 2007), eggshell membrane (Koumanova et al., 2002), gulmohar plant leaf powder (Ponnusami et al., 2009), teak leaf powder (Ponnusami and Srivastava, 2009), grape fruit peel (Saeeda et al., 2010), banana stalk (Bello et al., 2012), periwinkle shells (Bello and Ahmada, 2011), eggshell particles (Sarathi Guru and Dash, 2012) have been used for the removal of dyes from industrial effluents.

The interactions between low-cost adsorbents and dyes (adsorbates) are extensively studied through batch (Somasekhara Reddy et al., 2012; Fernandez et al., 2010; Zhang et al., 2012), equilibrium (Sun and Xu, 1997; Nassar and El-Geundi, 1991; Asfour et al., 1985 a,b) and column studies (Robinson et al., 2002; Han et al., 2007, 2008, 2009 ; Fernandez et al., 2010; Zhang et al., 2011a,b, 2012; Akara et al., 2011; Saha et al., 2012).

The Bengal gram seed husk (BGSH) is already used for the removal of a direct dye, congo red (CR) by using batch studies (Somasekhara Reddy et al., 2017a,b). SHBG is also used for the removal of different dyes like CR, MB, RB and AB through equilibrium studies to understand the removal capacity of the BGSH. Therefore, interest led us to use the same material for the removal of direct dyes like CR, DTB, and DB through column studies. In this paper, SHBG is used to remove different dyes like CR, DTB and DB from aqueous solution through column studies.

Adsorption isotherms were traditionally used for preliminary investigations and fixing the operational parameters. But in practice, the final technical systems normally use column type operations. Moreover, isotherms cannot give accurate scale-up data in a fixed bed system, so the practical applicability of products in column operation was investigated to obtain factual design models.

1.1. Theory of bed depth service time (BDST) model

The problem in designing adsorption columns is to predict how much effluent the bed will treat, or how long the bed will last before regeneration is necessary. All existing models are based on determining breakthrough curves for specific systems. Therefore, column operations are essential for industrial scale designing of technical systems. A number of models for the design of fixed bed adsorbers have been developed based on mathematical analysis and prediction of the shape of breakthrough curves.

A simplified approach for fixed bed adsorbers is available to correlate the service time, t, with the operation variables. Such a model is the Bed Depth Service Time (BDST) model (Hutchins, 1973; Dole and Klotz ,1946). The BDST (bed depth service time) model proposed by Hutchins (1973) is adopted for the design of fixed-bed adsorbers. It deals with the movement of an adsorption wave front through the adsorbent bed. The BDST has a linear relationship as given below

$$S_t = AB_d + \gamma \quad (1)$$

where

S_t = Bed service time (min)

$A = N_0/(C_0\, u)$ and $\gamma = [u/(K_0 N_0)][\ln(C_0/C_t) - 1]$

B_d = Bed depth (cm)

N_0 = Dynamic capacity by using column

K_0 = Rate constant of adsorption by using column (L/mg min)

u = Dye flow rate (ml/min)

By plotting service time S_t against bed depth from the experimental data, N_0 can be evaluated from the slope of the graph, and K_0 is obtained from the intercept at $S_t = 0$.

The service time of a column can be related to a number of process variables such as concentration of adsorbate, column height, flow of solution of adsorbate, pH of adsorbate solution and presence of foreign ions, size of the adsorbent and nature of adsorbate. However, at 50% breakthrough, the BDST model reduces to a form which predicts that a plot of BDST at 50% breakthrough against bed height should be a straight line passing through the origin. The critical bed depth is the point where the best-fit line through the data intersects the abscissa.

2. Materials and methods

2.1. Preparation of adsorbent, SHBG

The preparation of adsorbent is already explained in previous paper (Somasekhara Reddy et al., 2017a,b). However, the procedure is again given here. The seed husk of Bengal gram (SHBG) is discarded as a waste in a small-scale industry where dal of Bengal gram (which is used in the preparation of certain food items) is separated from seed of Bengal gram. This waste is used in certain areas as foodstuff to the animals in addition to use as fire wood in hotels and restaurants. The SHBG is collected from a local industry, which is in a nearby town, Nandyal and washed thoroughly with de-ionized water for removing dirt. The dried husk material is ground and sieved to desired mesh size like $53 < - < 75$ μm. It is abbreviated as SHBG. It is used as an adsorbent for the removal of dyes like CR, DTB and DB.

2.2. Adsorbate

CR, DTB and DB are obtained from M/S Sipka Sales Corporation, New Delhi free of cost and are used without further

purification. The wave length of the maximum absorbency for CR, DTB and DB is 497, 615 and 500 nm, respectively. The physical properties of selected dyes are shown in Table 1. The chemical structures of selected dyes are shown in Fig. 1.

Stock solution of 1000 mg L^{-1} was prepared by dissolving accurate quantity of the dye in double distilled water. The experimental solution was obtained by diluting the stock solution to the designed initial dye concentration.

2.3. Experimental

2.3.1. Methods of column studies

A weighed quantity of SHBG (53 < – < 75 μm) was made into a slurry with hot water and fed slowly into glass column (1.8–45 cm) with sintered disc and screw cock. The water already present in column was displaced to avoid air entrapment (Fornwalt and Hutchins, 1966). Water was slowly added to the SHBG material present in the column until the effluent was colourless. At this point, continuously the CR dye solution (50 mg L^{-1} except in effect of concentration of CR) was added from a separating funnel and a constant liquid level (around 10 cm liquid column above the SHBG) could be easily maintained by adjusting the flow rate from the separating funnel. The CR dye solution was percolating or diffusing through SHBG material downwards under gravity at flow rate of 10 ml per 15 min. The amount of CR dye adsorbed on SHBG could be calculated by measuring the absorbance of effluent from the column through the already prepared calibration curves. The effect of concentration of CR dye solution (25, 50, 75, and 100 mg L^{-1}), column height (3.5, 7.0, 10, and 12.5 cm), pH (5.6, 7.02, and 9.1), effect of SBP size (53 < – < 75, 75 < – < 90, 90 < – < 150 and > 150 μm), effect of similar dyes (CR, DTB, and DB) and effect of foreign ions (Sodium, Potassium, Calcium, and Magnesium) on adsorption of Congo red were studied at 3.5 cm column height and at 50 mg L^{-1} CR dye concentration.

2.3.2. Column regeneration

Column regeneration experiments were carried out in which SHBG loaded with CR was subjected to elution of CR with acetone. Simultaneously, the regeneration of the adsorbent, SBP material was also studied. Three regeneration experiments were performed. In the first experiment, acetone was added with 0.6667 ml min^{-1} to the 3.5 cm height exhausted column of SHBG in which 50 mg L^{-1} concentrated CR was passed. In the second experiment, acetone was added with 0.6667 ml min^{-1} to the 3.5 cm height exhausted column of SHBG in which 100 mg L^{-1} concentrated CR was passed. In the third experiment, acetone was added with 0.3333 ml min^{-1} to the 5 cm height exhausted column of SHBG in which 50 mg L^{-1} concentrated CR was passed.

3. Results and discussion

3.1. Characterization of the adsorbent

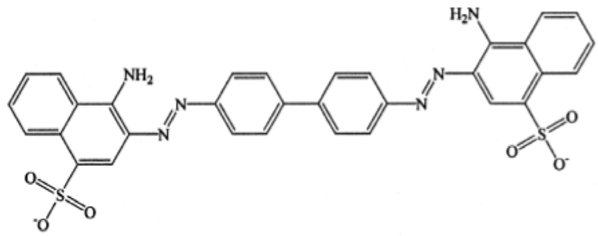
The characterization of the adsorbent, SHBG was done in the previous papers where the SHBG was used for removal of CR through batch kinetics experiments and equilibrium studies (Somasekhara Reddy et al., 2017a,b).

3.2. Effect of initial concentration of CR

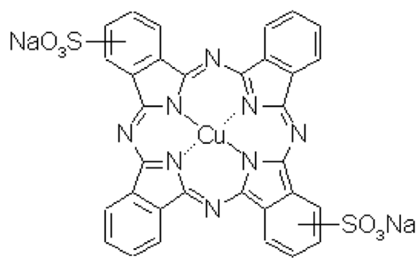
The effect of initial concentration of CR (25, 50, 75 and 100 mg L^{-1}) on the adsorption of CR in column containing SHBG was studied at a constant flow rate (0.67 ml min^{-1}), a constant particle size of SHBG (53 < – < 75), a constant cross sectional area of column (same column is used for all CR concentrations), constant pH of the CR solution (7.02) and constant height (3.5 cm). The experimental details like time taken for emerging first colourless drop and colour drop from the column are shown in Table 2. The breakthrough curves for all initial concentrations were drawn between the volume treated and C_t/C_0 as shown in Fig. 2. Higher $t_{1/2}$ is observed for the lowest concentration of 25 mg L^{-1} of CR and the order of decreasing $t_{1/2}$ was as follows 25 mg L^{-1} of CR (831.69 min) > 50 mg L^{-1} of CR (343.55 min) > 75 mg L^{-1} of CR (217.5 min) > 100 mg L^{-1} of CR (97.42 min). It is observed that the breakthrough time decreased with increasing inlet CR concentration. It was observed from Fig. 2 that the sharper breakthrough curves were obtained as the inlet concentration of CR increased. The larger the inlet concentration, the steeper is the slope of breakthrough curve and the smaller is the breakthrough time. The low initial CR concentration resulted in better adsorption into SHBG than the high initial CR concentration. This was because the former could be adsorbed more slowly through the SHBG. In other words the CR molecules were not adsorbed onto SHBG in a short time period at high initial CR concentration. It was confirmed further by the column capacity and the values are arranged in Table 2. A similar observation was made in case of adsorption of methylene blue on chemically modified wheat straw (Zhang et al., 2011a,b), adsorption of reactive black on granular activated carbon prepared from waste (Ahmad and Hameed, 2010), adsorption of methylene blue on phoenix tree leaf powder (Han et al., 2009) adsorption of DTB onto polyamide-epichlorohydrin-cellulose polymer (Hwang and Chen, 1993) and adsorption of brilliant yellow on cross-linked chitosan fibre (Yoshida and Takemori, 1997).

Table 1 Physical properties of the selected dyes.

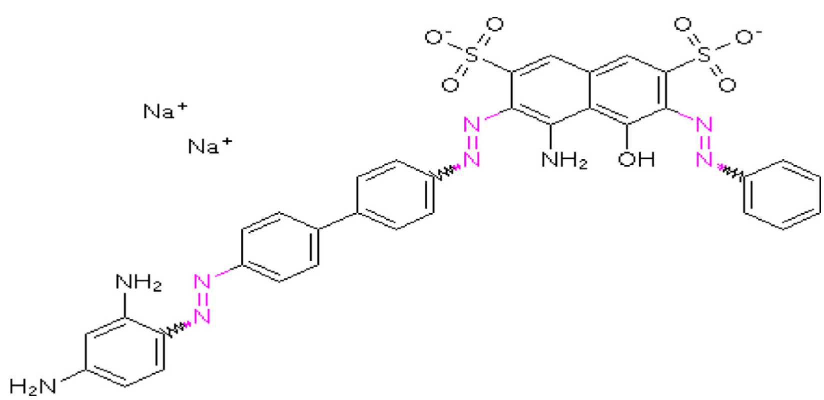
Dye	Properties				
	C.I. number	C.I. name	λ_{max} (nm)	Class	Mol. weight
CR	22120	Direct red 28	497	Polyazo	696.67
DTB	74180	Direct blue86	615	Trisazo	782.175
DB	30235	Direct black38	500	Triphenyl amine	781.73



Structure of Congo red (CR)



Structure of Direct Turquoise Blue-86 (DTB)



Structure of Direct Black 38 (DB)

Figure 1 Structures of Congo red (CR), Direct turquoise blue 86 (DTB) and Direct black 38 (DB).

Table 2 Column data at different concentrations of CR. Conditions: Flow rate = 0.667 ml min^{-1}; Time taken for the first colourless drop to emerge = 1 min; Column height = 3.5 cm; Mass of SHBG taken in a column = 2.0212 g; Size of SHBG = 53 < – < 75 μm; pH of CR solution = 7.01.

Concentration of CR (mg L^{-1})	Time taken for the first colour drop to emerge	$t_{1/2}$ (min)	Column capacity (mg g^{-1})
25	5 h 50 min	851.69	7.316
50	3 h 25 min	343.54	6.572
75	2 h 25 min	217.5	5.456
100	1 h 75 min	97.42	4.712

3.3. Effect of particle size of the adsorbent

The effect of SHBG particle size (53 < – < 75, 75 < – < 90, 90 < – < 150 and > 150 μm) on the adsorption of CR in column containing SHBG was studied at constant flow rate (0.667 ml min^{-1}), constant cross sectional area of column (same column is used for all particle sizes), constant initial concentration of CR solution (50 mg L^{-1}), constant pH of CR solution (pH 7.02) and constant height (3.5 cm). The experimental details like time taken for the first colourless drop and the colour drop emergence from the column are shown in Table 3. The breakthrough curves for all particle sizes were

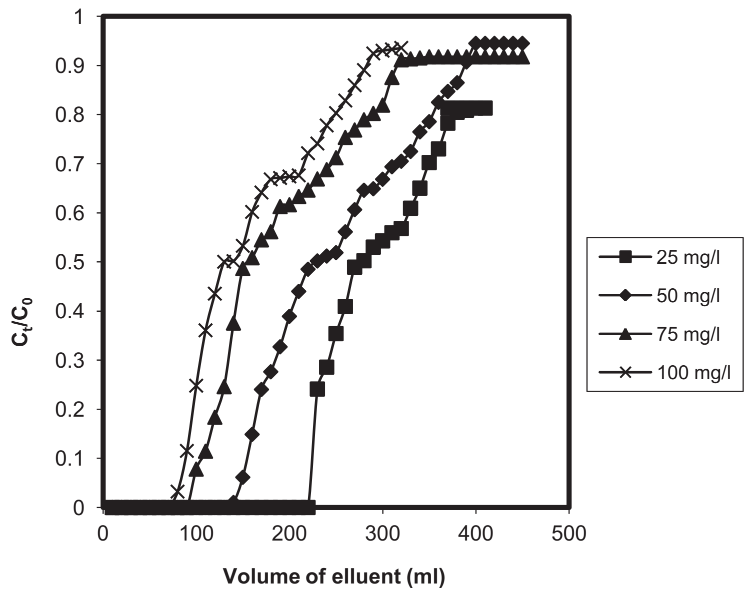


Figure 2 Breakthrough curve of the effect of influent concentration on CR adsorption on SHBG. Conditions: flow rate = 0.667 ml min^{-1}; size of SHBG ⩾ 53 < 75 μm; pH of CR solution = 7.01; column height = 3.5 cm.

Table 3 Column data at different sizes of SHBG. Conditions: C_0 = 50 mg L^{-1}. Remaining conditions in Table 2.

Size of SHBG (μm)	Time taken for the first colour drop to emerge	$t_{1/2}$ (min)	Column capacity (mg g^{-1})
53 < – < 75	3 h 25 min	343.55	6.572
75 < – < 90	1 h	186	4.216
90 < – < 150	45 min	126.39	3.720
> 150	15 min	96.65	3.224

drawn between the volume treated and C_t/C_0 as shown in Fig. 3. Higher $t_{1/2}$ is observed for the smaller sized particles of SHBG and the order of decreasing $t_{1/2}$ was as follows (53 < – < 75) size of SHBG (343.55 min) > (75 < – < 90) size of SHBG (186.00 min) > (90 < – < 150) size of SHBG (126.39 min) > (> 150) size of SHBG (96.65 min), respectively. This reveals that smaller size was favourable for high adsorption of CR. It was confirmed further by the column capacity and the values are arranged in Table 3. It was an expected trend only because a smaller particle provides more surface area. Fig. 3 shows that the breakthrough point curves shifted to the left when particle size increased. However, this shift was greater when the particle size increased from 53 < – < 75 μm to 75 < – < 90 μm than when it passed from 75 < – < 90 μm to 90 < – < 150 μm to > 150 μm. This similar trend was observed in equilibrium studies also (Somasekhara Reddy et al., 2017a,b). A close observation of the results reveals that $t_{1/2}$ was becoming closer at higher sizes. Probably, at more higher sizes, $t_{1/2}$ may be the constant due to less surface area available. A similar observation was made in case of biosorption of reactive black 5 on chitosan (Barron-Zambrano et al., 2010), adsorption of astrazone blue on wood (Poots et al., 1978) and the adsorption of DTB on polyamide-epichlorohydrin-cellulose polymer (Hwang and Chen, 1993).

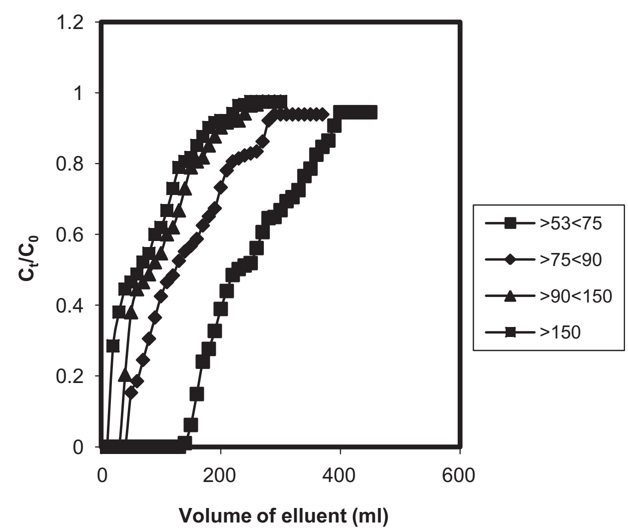


Figure 3 Breakthrough curve of the effect of size of SHBG on CR adsorption on SHBG. Conditions: flow rate = 0.667 ml min^{-1}; influent concentration of CR = 50 mg L^{-1}; pH of CR solution = 7.01; column height = 3.5 cm.

3.4. Effect of pH

The effect of pH (5.6, 7.02 and 9.1) of CR solution on the adsorption of CR in column containing SHBG was studied at a constant flow rate (0.667 ml min^{-1}), a constant particle size of SHBG (53 < – < 75 μm), a constant cross sectional area of column (same column is used for all pHs), a constant initial concentration CR solution (50 mg L^{-1}) and a constant height (3.5 cm). The experimental details like time taken for the first colourless drop and the colour drop emergence from the

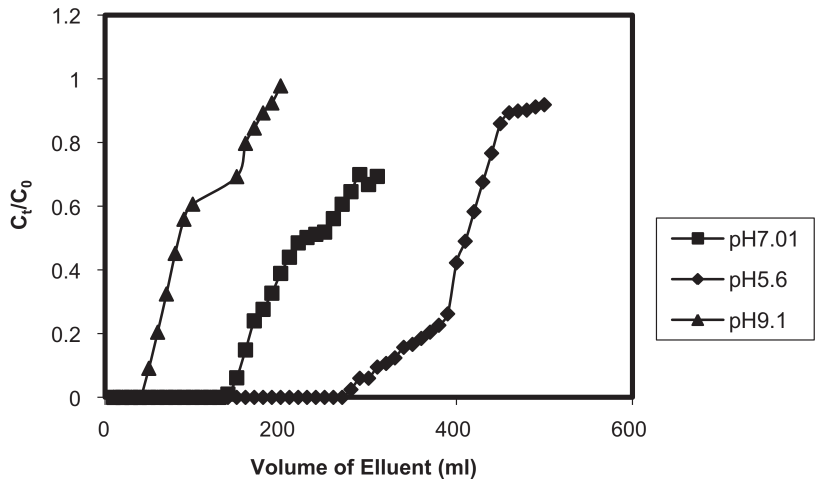


Figure 4 Breakthrough curve of the effect of pH of CR solution on CR adsorption on SHBG. Conditions: flow rate = 0.667ml min^{-1}; influent concentration of CR = 50 mg L^{-1}; influent concentration of CR = 50 mg L^{-1}; size of SHBG $\geqslant 53 < 75$ μm; column height = 3.5 cm.

column are shown in Table 4. The breakthrough curves for all pHs of solutions of CR were drawn between the volume treated and C_t/C_0 as shown in Fig. 4.

Higher $t_{1/2}$ is observed for the lower pH of CR solution and the order of decreasing $t_{1/2}$ was as follows pH 5.6 of CR solution (627.21 min) > pH 7.02 of CR solution (343.55 min) > pH 9.1 of CR solution (92.31 min). It was confirmed further by the column capacity and the values are arranged in Table 4. This reveals that lower pH is favourable for the removal of CR by using SHBG. This may be due to the interaction between more positive CR ion and the more negative SHBG due to acquiring a positive charge by the cellulose present in SHBG as it was in contact with water. This similar trend was observed in kinetics and equilibrium studies also (Somasekhara Reddy et al., 2017a,b). As shown in Fig. 4 with an increase of pH in the influent, the breakthrough curves shifted from right to left, which indicated that less CR was removed. The adsorption capacity of SHBG would decrease with an increase in pH of GR solution. It requires less time to reach the saturation, and the efficiency of biosorption was much lower. A similar observation was made in case of adsorption of brilliant yellow on cross-linked chitosan fibre (Yoshida and Takemori, 1997). It was observed contrary to this that the adsorption of methylene blue (MB) on rice husk was increased with an increase in pH of MB solution (Han et al., 2007)

3.5. Effect of dyes

The effect of similar type of dyes like DTB and DB (both are direct dyes because CR is also direct dye) on the adsorption of CR in column containing SHBG was studied at constant flow rate (0.67 ml min^{-1}), constant particle size of SHBG ($53 < - < 75$ μm), constant cross sectional area of column (same column is used for all dyes), constant pH of the CR solution (7.02), constant height (3.5 cm) and at constant influent dye, DTB/DB/CR concentration (50 mg L^{-1}). The experimental details like time taken for the first colourless drop and the colour drop emergence from the column are shown in Table 5. The breakthrough curves for all the combinations were drawn between the volume treated and C_t/C_0 as shown in Fig. 5. The more service time at which 50% breakthrough was achieved ($t_{1/2}$) was observed for the CR and the order of decreasing

Table 4 Column data at different pH of CR solutions. Conditions: C_0 = 50 mg L^{-1}. Remaining conditions in Table 2.

pH	Time taken for the first colour drop to emerge	$t_{1/2}$ (min)	Column capacity (mg g^{-1})
5.6	7 h 15 min	627.21	9.548
7.01	3 h 25 min	343.54	6.572
9.1	1 h	92.31	2.976

Table 5 Column data for different dyes. Conditions: C_0 = 50 mg L^{-1}. Remaining conditions in Table 2.

Dyes	Time taken for the first colour drop to emerge	$t_{1/2}$ (min)	Column capacity (mg g^{-1})
CR	3 h 25 min	343.54	6.572
DTB	15 min	21.07	1.984
DB	3 min	53.41	1.612

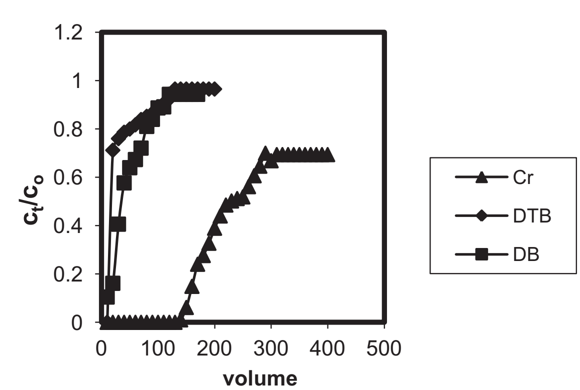


Figure 5 Breakthrough curve of the effect of different direct dyes on dye adsorption on SHBG. Conditions: flow rate = 0.667 ml min^{-1}; influent concentration of dyes = 50 mg L^{-1}; size of SHBG $\geqslant 53 < 75$ μm; column height = 3.5 cm.

$t_{1/2}$ is as follows CR (343.55 min) > DB (53.41 min) > DTB (21.07 min). Therefore, SHBG was capable to remove CR effectively compared to DB and DTB even though the CR, DB and DTB belong to the same type of dyes (direct dyes). It is confirmed further by the column capacity and the values are arranged in Table 5. The low uptake is possibly due to the fact that the DB and DTB have much larger dye molecules and a long chain than the CR, so that it could not penetrate the internal pore structure of the SHBG particles. As shown in Fig. 5, breakthrough curves shifted from right to left, for CR, DB and DTB, respectively. The adsorption capacity of SHBG would decrease for DB and DTB. DB and DTB require less time to reach the saturation when compared with CR, and the efficiency of biosorption was much lower for DB and DBT. The absorption of direct red 83 in the column contains polyamide-epichlorohydrin-cellulose polymer was less compare to the adsorption of DTB and direct red 83 on the same material because direct red 83 is larger than that of DTB and direct red 83 (Hwang and Chen, 1993).

3.6. Effect of foreign ions

For the determination of any interference caused by the presence of other inorganic cations, monovalent sodium (Na) and potassium (K), and divalent calcium (Ca) and magnesium (Mg) were added to the CR solution passed through the column for adsorption studies. These elements are major constituents of saline and hard waters and are likely to be encountered in most industrial effluents from which dyes are intended to be removed by these column studies. Not only that in the dye manufacturing process, salts are usually discharged into the wastewater for their salting-out effect. Many ions are present in the dye-house wastewater. Therefore, the influence of foreign ions was studied in this paper.

The influence of foreign ions like Na, K, Ca and Mg on the adsorption of CR in column containing SHBG was studied at a constant flow rate (0.667 ml min^{-1}), a constant particle size of SHBG (53 < – < 75 μm), a constant cross sectional area of column (same column is used for all foreign ions), a constant initial concentration CR solution (50 mg L^{-1}) and a constant height (3.5 cm). The concentrations of NaCl, KCl, $CaCl_2$ and $MgSO_4$ salts in the present experiments were 1, 1, 0.5 and 0.5 M, respectively. The experimental details like time taken for the first colourless drop and the colour drop emergence from the column are shown in Table 6. The breakthrough curves for CR in the presence of foreign ions were drawn between the volume treated and C_t/C_0 as shown in Fig. 6. Higher $t_{1/2}$ is observed for the presence of monovalent ion, potassium along with CR (CR-K) and the order of decreasing $t_{1/2}$ is as follows CR-K (540.82 min) > CR-Mg (473.83 min) > CR-Ca (403.28 min) > CR-Na (384.67 min) > CR alone (343.55 min). It was confirmed further by the column capacity and the values are arranged in Table 6. This reveals that the presence of either monovalent ion or divalent ion increases adsorption of CR. The enhancement of adsorption caused by salts was also documented (Han et al., 2008; Jeng 1992; Randtke and Jepsen, 1982; Verwey and Overbeek, 1948) in the literature. A similar trend was observed in case of adsorption of CR on rice husk (Han et al., 2008), adsorption of basic red 46, basic red 18 and basic red 28 on activated clay (Hsu et al., 1997), adsorption of direct orange 39 (McKay, 1982a,b), adsorption of phenol (Cooney 1998), adsorption of p-nitrophenol (Snoelyink et al., 1969), adsorption of sodium benzene sulphonate (Coughlin and Tan, 1968) and various organic compounds (benzoic acid, aniline, m-phenylenediamine and anthranilic acid) (Cooney and Wijaya, 1987) on activated carbon in the presence of NaCl, Na_2SO_4, NaCl, NaCl, $CaCl_2$ and NaCl respectively when organic compounds are fully ionized. It is thought that the presence of salts, electrolytes, the charge density in the diffusion layer is significantly increased, which in turn minimizes the volume of diffusion

Table 6 Column data for different foreign ions. Conditions: C_0 = 50 mg L^{-1}. Remaining conditions in Table 2.

Foreign ions	Time taken for the first colour drop to emerge	$t_{1/2}$ (min)	Column capacity (mg g^{-1})
CR-Na	2 h 15 min	384.69	5.952
CR-K	4 h	540.82	8.308
CR-Ca	2 h	403.28	5.580
CR-Mg	1 h 45 min	473.83	6.448

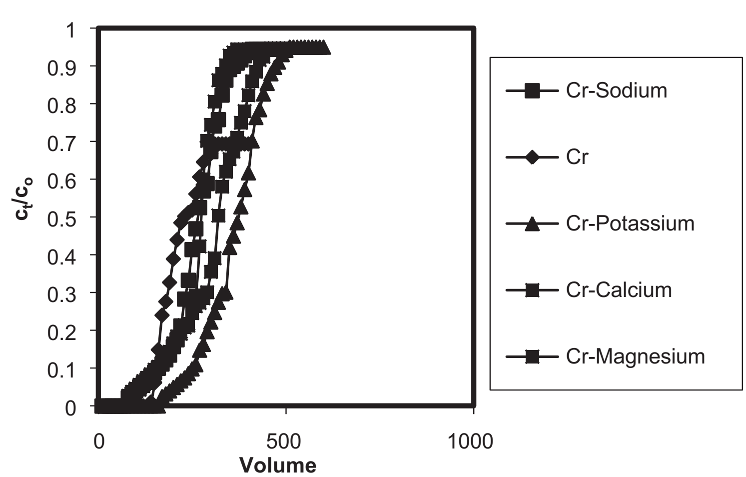


Figure 6 Breakthrough curve of the effect of different foreign ions on CR adsorption on SHBG. Conditions: flow rate = 0.667 ml min^{-1}; influent concentration of dyes = 50 mg L^{-1}; size of SHBG ⩾ 53 < 75 μm; column height = 3.5 cm.

layer required to neutralize the surface charge. These cations have a thinning effect on the diffusion layer formed on the surface of the particles. Although the total net charge did not change, the thickness of the diffusion layer had diminished significantly (Benefield et al., 1982). Further the more complex structure of CR would indicate a more complex charge distribution throughout its structure making it more prone to adsorption.

The adsorption of CR was more in the presence of KCl compared to other salts. Probably the diffusion layer thickness may be further reduced in the presence of KCl. The variation of concentrations of salts may further increase the adsorption capacity.

The adsorption of methylene blue in the presence of salts (NaCl and $CaCl_2$) onto rice husk was decreasing (Han et al., 2007) instead of an increase in case of adsorption of CR on the same rice husk in the presence of NaCl (Han et al., 2008).

3.7. Effect of height

The effect of bed depth of the column (3.5, 7, 10 and 12.5 cm) on the adsorption of CR in column containing SHBG was studied at a constant flow rate (0.67 ml min^{-1}), a constant particle size of SHBG (53 < – < 75 μm) a constant cross sectional area of column (same column is used for all bed depths), a constant initial concentration CR solution (50 mg L^{-1}) and a constant pH of CR solution (7.08). The experimental details like time taken for the first colourless drop and the colour drop emergence from the column are shown in Table 7. The breakthrough curves for all bed depths were drawn between the volume treated and C_t/C_0 as shown in Fig. 7.

Table 7 Column data for different heights. Conditions: C_0 = 50 mg L^{-1}. Remaining conditions in Table 2.

Column height (cm)	Time taken for the first colour drop to emerge	$t_{1/2}$ (min)	Column capacity (mg g^{-1})
3.5	3 h 25 min	343.54	6.572
7.0	6 h 5 min	547.86	4.712
10.0	9 h	739.52	4.474
12.5	12 h	957.45	4.518

Higher $t_{1/2}$ was observed for the higher bed depth and the order of decreasing $t_{1/2}$ was as follows, 12.5 cm (957.45 min) > 10 cm (739.52 min) > 7.0 cm (547.86 min) > 3.5 cm bed depth of column (343.54 min). It was confirmed further by the column capacity and the values are arranged in Table 7. This reveals that higher bed depth was favourable for the removal of CR by using SHBG. So the higher bed depth of column resulted in a decrease in the solution concentration in the effluent at the same time. The slope of breakthrough curve decreased with increasing bed depth, which resulted in a broadened mass transfer zone. Higher uptake was observed at the highest bed depth due to an increase in the surface area of the biosorbent, SHBG, which provided more binding sites for the sorption (Han et al., 2007, 2008, 2009; Sivakumar and Palanisamy, 2009a,b; Singh et al., 2009; Tan et al., 2008).

3.7.1. Bed depth service time (BDST) model

BDST model was used to describe the fixed-bed column behaviour and to extend the laboratory experiments for industrial applications. The BDST model proposed by Hutchins (1973) states that the service time of a column can be related to a number of process variables. However, in the present studies the service time at which 50% breakthrough is achieved ($t_{1/2}$) is related to the height. The experimental data in column were fitted through BDST model (Eq. (1)). The plot is made between bed depth and the service time, $t_{1/2}$ and the plot is shown in Fig. 8. The straight line is observed in Fig. 8. The dynamic capacity, N_0 of SBP for CR was calculated from the slope of Fig. 8 and it was arranged in Table 8. The dynamic capacity of SHBG for removal of CR is 2244.33 mg ml^{-1}.

3.8. Effect of regeneration

Recovery of adsorbate material (CR) as well as the regeneration of adsorbent is an important process in wastewater treatment.

The SHBG gets exhausted on continuous usage of the same for column studies. At this point, the concentration of influent (dye solution pouring into the column) is equal to the concen-

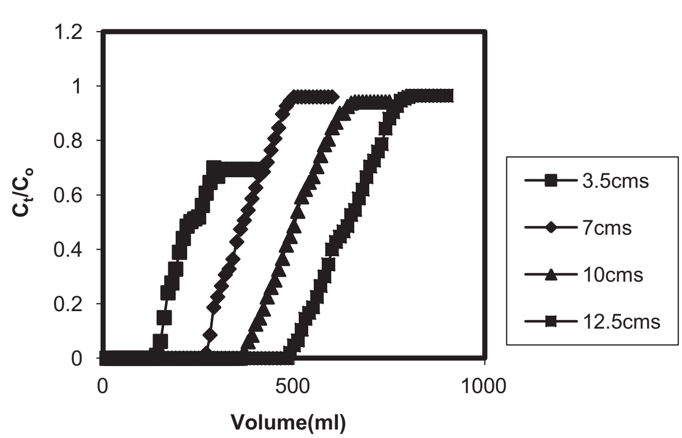


Figure 7 Breakthrough curve of the effect of different column heights on CR adsorption on SHBG. Conditions: flow rate = 0.667 ml min^{-1}; influent concentration of dyes = 50 mg L^{-1}; size of SHBG = > 53 < 75 μm; column height = 3.5 cm.

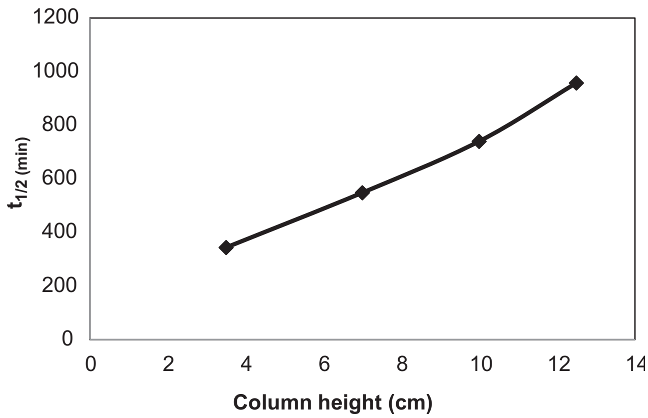


Figure 8 Analysis of BDST model.

Table 8 Analysis of results of BDST model.

Column height (cm)	Time taken for the first colour drop to emerge	N_0 (mg L^{-1})	R^2
3.5	3 h 25 min	2244.3	0.9917
7.0	6 h 5 min		
10.0	9 h		
12.5	12 h		

tration of effluent (dye solution coming out from the column). Therefore, the recovery of the adsorbed material (dyes) as well as regeneration of the SHBG becomes quite necessary. Thermal regeneration is not possible in our case as we are using SHBG without any modification. Elution of dye with simultaneous chemical regeneration by a suitable solvent is a definite alternative to thermal regeneration and is tried with the help of acetone in these investigations.

The exhausted column of SHBG which was loaded with CR was regenerated with acetone. Acetone was added to the exhausted column with 10 ml increments for all the experiments till the regeneration was completed. In the first experiment, acetone was added with 0.6667 ml/min to the 3.5 cm height exhausted column of SHBG in which 50 mg L^{-1} concentrated CR is passed. 120 ml of acetone is required for the completion of regeneration of this column and the total amount of CR was recovered in this case. In the second experiment, acetone is added with 0.6667 ml min^{-1} to the 3.5 cm height exhausted column of SHBG in which 100 mg L^{-1} concentrated CR was passed. 80 ml of acetone is required for the completion of regeneration of this column and the total amount of CR was recovered in this case also. In the third experiment, acetone was added with 0.3333 ml min^{-1} to the 5.0 cm height exhausted column of SHBG in which 50 mg L^{-1} concentrated CR was passed. 120 ml of acetone was required for the completion of regeneration of this column and the total amount of CR was recovered in this case. The regeneration curves are shown in Fig. 9. The results reveal that the regeneration of CR was almost the same for different flow rates. At the beginning more amount of CR was eluted due to more accumulation of CR.

After de-sorption, the columns of SHBG were washed with 100 ml of hot water in 10 ml fractions at the same flow rate which is maintained for the flow of dye. These columns are again loaded with the two different concentrations (50 mg L^{-1} and 100 mg L^{-1}) of CR solution at the flow rate of 0.6667 ml min^{-1} to check the adsorption efficiency of the SHBG. After regeneration the column is exhausted early. It is known from the $t_{1/2}$ values and the values are shown in Table 9. The data may be helpful in designing a fixed bed column for the treatment of dye of known concentrations.

3.9. Cost estimation

Basically, India is an agricultural country. The disposal of the solid agricultural wastes/by-product, SHBG is a big problem and it creates a lot of pollution problems. Therefore, using this waste material, SHBG for the useful wastewater treatment purpose is appreciable and these materials are/will be supplied free of cost by the agriculturists because they want to get rid of them. The cost involved is only for transportation and process of the collected material.

The selected agricultural waste/by-product, SHBG was procured free of cost or very less cost and the average and approximate cost of the materials is Rs. 25/- per ton. The cost which includes transport, process charges etc. of the final material

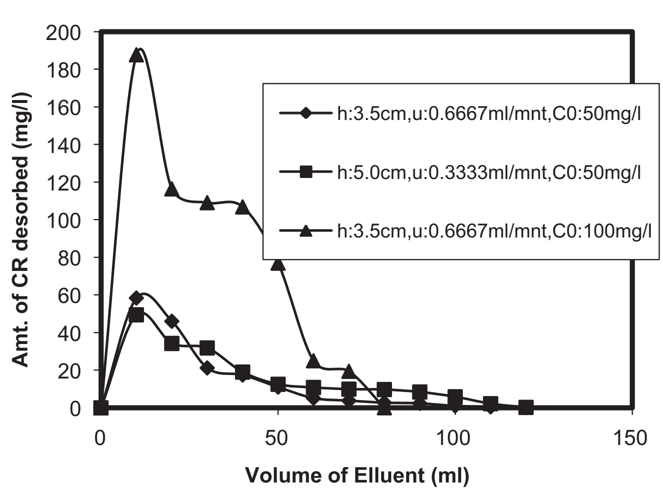


Figure 9 Desorption curve of CR from SHBG.

Table 9 Column data for regeneration. Conditions: $C_0 = 50$ mg L^{-1}. Remaining conditions in Table 2.

Concentration of CR (mg L^{-1})	Column height (cm)	Time taken for the first colour drop to emerge	$t_{1/2}$ (min)	Column capacity (mg g^{-1})
50	3.5 (before)	3 h 25 min	343.54	6.572
	3.5 (after)	2 h 20 min	180.09	5.208
100	3.5 (before)	2 h 15 min	150.4	4.836
	3.5 (after)	1 h 30 min	120.35	4.216
	5 (before)	4 h 20 min	224.36	4.960

which was used for the adsorption studies was Rs. 150/- per ton. The cost of final material was nothing when compared to the cost of activated carbon. Of course, the final cost estimation was also based on the removal capacity of different dyes and on regeneration. Even the regeneration of exhausted SHBG was not that much efficient, still the process was economical as compared to carbon because of low cost and abundant availability of SBP. The cost estimation of some agricultural wastes/by-products was available in the literature (Somasekhara Reddy et al., 2012; Asfour et al., 1985; Nassar et al., 1991; Hameed et al., 2008).

4. Conclusions

In the present study, SHBG packed bed has been used to analyse the column dynamics in the adsorption process. The influence of the bed height or bed depth (B_d), inlet CR concentration (C_0), size of SHBG, pH of CR solution and regeneration of CR or desorption of CR from the surface of SHBG on breakthrough curves have been investigated. Higher uptake of CR was observed at higher bed depth. It was found that the time to breakthrough decreased with an increase in C_0. The larger the C_0, the steeper was the slope of the breakthrough curve. A 50% breakthrough curve between $t_{1/2}$ and B_d must result in a straight line passing through the origin, however, the straight line does not pass through the origin. The plot of 50% breakthrough ($t_{1/2}$) versus B_d curve did not pass through the origin indicating the adsorption of CR onto SHBG occured through complex mechanism. Dynamic adsorption capacity (N_0) as calculated from the slope of 50% plot was 2244.33 mg ml^{-1}.

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References

Ahmad, A.A., Hameed, B.H., 2010. Fixed-bed adsorption of reactive azo dye onto granular activated carbon prepared from waste. J. Haz. Mat. 175, 298–303.

Ahmad, R., Kumar, Rajeev., 2010. Adsorption studies of hazardous malachite green onto treated ginger waste. J. Environ. Manage. 91, 1032–1038.

Akara, S.T., Gorgulub, A., Akara, T., Celikc, S., 2011. Decolorization of reactive blue 49 contaminated solutions by capsicum annuum seeds: batch and continuous mode biosorption applications. Chem. Eng. J. 168, 125–133.

Alila, S., Boufi, S., 2009. Removal of organic pollutants from water by modified cellulose fibres. Ind. Crops Prod. 30, 93–104.

Amela, K., Hassena, M.A., Kerroum, D., 2012. Isotherm and kinetics study of biosorption of cationic dye onto banana peel. Energy Procedia 19, 286–295.

Asgher, M., Bhatti, H.N., 2012. Evaluation of thermodynamics and effect of chemical treatments on sorption potential of citrus waste biomass for removal of anionic dyes from aqueous solutions. Ecol. Eng. 38, 79–85.

Asfour, H.M., Fadali, O.A., Nassar, M.M., El-Geundi, M.S., 1985. Equilibrium studies on adsorption of basic dyes on hardwood. J. Chem. Technol. Biotechnol. 35A, 21–27.

Bello, O.S., Ahmada, M.A., Ahmada, N., 2012. Adsorptive features of banana (*Musa paradisiaca*) stalk-based activated carbon for malachite green dye removal. Chem. Ecol. 28, 153–167.

Bello, O.S., Ahmada, M.A., 2011. Removal of remazol brilliant violet-5R dye using periwinkle shells. Chem. Ecol. 27, 481–492.

Benefield, L.D., Judkins, J., Weand, B.L., 1982. Process Chemistry for Water and Wastewater Treatment. Prentice-Hall, Englewood Cliffs, New Jersey.

Bhattacharyya, K.G., Sharma, A., 2004. Azadirachta indica leaf powder as an effective biosorbent for dyes: a case study with aqueous congo Red solutions. J. Environ. Manage. 71, 217–229.

Binupriya, A.R., Sathishkumar, M., Jung, S.H., Song, S.H., Yun, S.I., 2009. A novel method in utilization of bokbunja seed wastes from wineries in liquid-phase sequestration of reactive blue 4. Int. J. Environ. Res. 3, 1–12.

Barron-Zambrano, J., Szygula, A., Ruiz, M., Maria Sastre, A., Guibal, E., 2010. In biosorption of reactive black 5 from aqueous solutions by chitosan: column studies. J. Envron. Manag. 91, 1–7.

Cooney, D.O., 1998. Adsorption Design for Wastewater Treatment. Lewis Publishers, Washington, DC, pp. 29–36.

Cooney, D.O., Wijaya, J., 1987. Effect of pH and added salts on the adsorption of ionizable organic species onto activated carbon from aqueous solution. In: Liapis, A.I. (Ed.), Processing of the Second Engineering Foundation Conference on Fundamentals of Adsorption. Engineering Foundation, New York, pp. 185–194.

Coughlin, R.W., Tan, R.N., 1968. Role of functional groups in adsorption of organic pollution on carbon. Chem. Eng. Programme Symp. Serv. 90, 207.

Dole, M., Klotz, I.M., 1946. Sorption of chloropicrin and phosgene on charcoal from a flowing gas stream. Ind. Eng. Chem. 38, 1289–1297.

Fernandez, M.E., Nunell, G.V., Bonellia, P.R., Cukierman, A.L., 2010. Effectiveness of Cupressus sempervirens cones as biosorbent for the removal of basic dyes from aqueous solutions in batch and dynamic modes. Bioresour. Technol. 101, 9500–9507.

Fornwalt, H.J., Hutchins, R.A., 1966. Purifyng liquids with activated carbon. Chem. Eng. J. 73, 179.

Gonga, R., Zhonga, K., Hua, Y., Chenb, J., Zhua, G., 2008. Thermochemical esterifying citric acid onto lignocellulose for

enhancing methylene blue sorption capacity of rice straw. J. Environ. Manage. 88, 875–880.

Gupta, V.K., Mittal, A., Kurup, L., Mittal, J., 2006. Adsorption of a hazardous dye, erythrosine, over hen feathers. J. Colloid Interface Sci. 304, 52–57.

Hameed, B.H., Mahmoud, D.K., Ahmad, A.L., 2008. Equilibrium modeling and kinetic studies on the adsorption of basic dye by a low-cost adsorbent: coconut (*Cocos nucifera*) bunch waste. J. Hazard. Mater. 158, 65–72.

Han, R., Ding, D., Xu, Y., Zou, W., Wang, Y., Li, Y., Zou, L., 2008. Use of rice husk for the adsorption of congo red from aqueous solution in column mode. Bioresour. Technol. 99, 2938–2946.

Han, R., Wang, Y., Zhao, X., Wang, Y., Xie, F., Cheng, J., Tang, M., 2009. Adsorption of methylene blue by phoenix tree leaf powder in a fixed-bed column: experiments and prediction of breakthrough curves. Desalination 245, 284–297.

Han, R., Wang, Y., Yu, W., Zou, W., Shi, J., Liu, H., 2007. Biosorption of methylene blue from aqueous solution by rice husk in a fixed-bed column. J. Haz. Mat. 141, 713–718.

Hsu, Y.C., Chiang, C.C., Yu, M.F., 1997. Adsorption behavior of basic dyes on activated clay. Sep. Sci. Technol. 32, 2513–2534.

Hirata, M., Kawasaki, N., Nakamura, T., Matsumoto, K., Kabayama, M., Tamura, T., Tanada, S., 2002. Adsorption of dyes onto carbonaceous materials produced from coffee grounds by microwave treatment. J. Colloid Interface Sci. 254, 17–22.

Hutchins, R.A., 1973. New simplified design of activated carbons systems. J. Am. Chem. Eng. 80, 133.

Hwang, M.C., Chen, K.M., 1993. The removal of color from effluents using polyamide- Epichlorohydrin-Cellulose polymer. I. Preparation and use in direct dye removal. J. Appl. Polym. Sci. 48, 299–311.

Jaikumar, V., Sathish Kumar, K., Gnana Prakash, D., 2009. Biosorption of acid dyes using spent brewery grains: characterization and modeling. Int. J. Appl. Sci. Eng. 7, 115–125.

Jeng, H.Y., 1992. The mechanism and phenomenon of stimulant wastewater of emulsified fatty acid and dye, Textile dyeing treated with activated clay (MS Thesis). Department of Chemical Engineering, National Taiwan Institute of Technology, Taipei, ROC.

Koumanova, B., Peeva, P., Allen, S.J., Galagher, K.A., Healy, M.G., 2002. Biosorption from aqueous solutions by eggshell membranes and *Rhizopus oryzae*: equilibrium and kinetic studies. J. Chem. Technol. Biotechnol. 77, 539–545.

Lakshmi, U.R., Srivastava, V.C., Mall, I.D., Lataye, D.H., 2009. Rice husk ash as an effective adsorbent: evaluation of adsorptive characteristics for indigo Carmine dye. J. Environ. Manage. 90, 710–720.

McKay, G., 1982a. Adsorption of dyestuffs from aqueous solutions with activated carbon I: equilibrium and batch contact-time studies. J. Chem. Technol. Biotechnol. 32, 759–772.

McKay, G., 1982b. Adsorption of dyestuffs from aqueous solutions with activated carbon II: column studies and simplified design models. J. Chem. Technol. Biotechnol. 32, 773–780.

Mittal, A., 2006. Adsorption kinetics of removal of a toxic dye, malachite Green, from wastewater by using hen feathers. J. Hazard. Mater. B133, 196–202.

Murugan, T., Ganapathi, A., Valliappan, R., 2010. Removal of dyes from Aqueous Solution by adsorption on biomass of mango (*Mangifera Indica*) leaves. E-J. Chem. 7, 669–676.

Nassar, M.M., El-Geundi, M.S., 1991. Comparative cost of colour removal from textile effluents using natural adsorbents. J. Chem. Technol. Biotechnol. 50, 257–264.

Noroozi, B., Sorial, G.A., Bahrami, H., Arami, M., 2007. Equilibrium and kinetic adsorption study of a cationic dye by a natural adsorbent—silkworm pupa. J. Hazard. Mater. B139, 167–174.

Ponnusami, V., Gunasekar, V., Srivastava, S.N., 2009. Kinetics of methylene blue removal from aqueous solution using gulmohar (*Delonix regia*) plant leaf powder: multivariate regression analysis. J. Hazard. Mater. 169, 119–127.

Ponnusami, V., Srivastava, S.N., 2009. Studies on application of teak leaf powders for the removal of color from synthetic and industrial effluents. J. Hazard. Mater. 169, 1159–1162.

Poots, V.J.P., McKay, G., Healy, J.J., 1978. Removal of basic dye from effluent using wood as an adsorbent. J. Water Pollut. Control Fed. 50, 926–935.

Randtke, S.J., Jepsen, C.P., 1982. Effects of salts on activated carbon adsorption of fulric acids. J. Am. Water Works Assoc. 74, 84–93.

Ray, P.K., 1986. Environmental pollution and cancer. J. Sci. Ind. Res. India 45, 370–371.

Robinson, T., Chandran, B., Sathya Naidu, G., Nigam, P., 2002. Studies on the removal of dyes from a synthetic textile effluent using barley husk in static-batch mode and in a continuous flow, packed-bed, reactor. Bioresour. Technol. 85, 43–49.

Saeeda, A., Sharif, M., Iqbala, M., 2010. Application potential of grapefruit peel as dye sorbent: kinetics, equilibrium and mechanism of crystal violet adsorption. J. Hazard. Mater. 179, 564–572.

Saha, P.D., Chakraborty, S., Chowdhury, S., 2012. Batch and continuous (fixed-bed column) biosorption of crystal violet by *Artocarpus heterophyllus* (jackfruit) leaf powder. Colloids Surf., B 92, 262–270.

Sanchez-Martin, J., Beltran-Heredia, J., Gragera-Carvajal, J., 2011. Caesalpinia spinosa and *Castanea sativa* tannins: a new source of biopolymers with adsorbent capacity. Preliminary assessment on cationic dye removal. Ind. Crops Prod. 34, 1238–1240.

Sarathi Guru, P., Dash, S., 2012. Eggshell particles (ESP) as potential adsorbent for styryl pyridinium dyes—a kinetic and thermodynamic study. J. Dispersion Sci. Technol. 33, 1012–1020.

Singh, S., Srivastava, V.C., Mall, I.D., 2009. Fixed-bed study for adsorption removal of furfural by activated carbon. Colloids Surf. A 332, 50–56.

Sivakumar, P., Palanisamy, P.N., 2009a. Packed bed column studies for the removal of acid blue 92 and basic red 29 using non-conventional adsorbent. Indian J. Chem. Technol. 16, 301–307.

Sivakumar, P., Palanisamy, P.N., 2009b. Adsorptive removal of reactive and direct dyes using non-conventional adsorbent – column studies. J. Sci. Ind. Res. 68, 894–899.

Snoelyink, V.L., Weber Jr., W.J., Mark Jr., H.B., 1969. Sorption of phenol and nitrophenol by active carbon. Environ. Sci. Technol. 3, 918–926.

Somasekhara Reddy, M.C., Sivarama Krishna, L., Varada Reddy, A., 2012. The use of an agricultural waste material, jujuba seeds for the removal of anionic dye (congo red) from aqueous medium. J. Haz. Mats. 203–204, 118–127.

Somasekhara Reddy, M.C., Nirmala, V., 2017a. Bengal Gram Seed Husk as a adsorbent for the removal of dyes from aqueous solutions – Batch studies. Arab. J. Chem. 10, S2554–S2566.

Somasekhara Reddy, M.C., Nirmala, V., Ashwini, C., 2017b. Bengal Gram Seed Husk as a adsorbent for the removal of dyes from aqueous solutions – Equilibrium studies. Arab. J. Chem. 10, S2406–S2416.

Sun, G., Xu, X., 1997. Sunflower stalks as adsorbents for color removal from textile wastewater. Ind. Eng. Chem. Res. 36, 808–812.

Tamez Uddin, Md., Rukanuzzaman, Md., Maksudur Rahman Khan, Md., Akhtarul Islam, Md., 2009. Adsorption of methylene blue from aqueous solution by jackfruit (*Artocarpus heterophyllus*) leaf powder: a fixed-bed column study. J. Environ. Manage. 90, 3443–3450.

Tan, I.A.W., Ahmad, A.L., Hameed, B.H., 2008. Adsorption of basic dye using activated carbon prepared from oil palm shell: batch and fixed bed studies. Desalination 225, 13–28.

Vankar, P.S., Sarswat, R., Dwivedi, A.K., Sahu, R.S., 2013. An assessment and characterization for biosorption efficiency of natural dye waste. J. Clean. Prod. 60, 65–70.

Verwey, E.J.W., Overbeek, J.T.G., 1948. Theory of the Stability of Lyophobic Colloids. Elsevier Scientific, Amsterdam, Netherlands.

Walsh, G.E., Bahner, L.H., 1980. Environ. Pollut. Ser. A 21, 169–179.

Wang, L., 2012. Application of activated carbon derived from 'waste' bamboo culms for the adsorption of azo disperse dye: kinetic, equilibrium and thermodynamic studies. J. Environ. Manage. 102, 79–87.

Yoshida, H., Takemori, T., 1997. Adsorption of direct dye on cross-linked chitosan fiber breakthrough curve. Water Sci. Technol. 35, 29–37.

Zhang, Z., O'Hara, I.M., Kent, G.A., Doherty, W.O.S., 2013. Comparative study on adsorption of two cationic dyes by milled sugarcane bagasse. Ind. Crops Prod. 42, 41–49.

Zhang, W., Li, H., Kan, X., Dong, L., Yan, H., Jiang, Z., Yang, H., Li, A., Cheng, R., 2012. Adsorption of anionic dyes from aqueous solutions using chemically modified straw. Bioresour. Technol. 117, 40–47.

Zhang, W., Yan, H., Li, H., Jiang, Z., Dong, L., Kan, X., Yang, H., Li, A., Cheng, R., 2011a. Removal of dyes from aqueous solutions by straw based adsorbents: batch and column studies. Chem. Eng. J. 168, 1120–1127.

Zhang, W., Dong, L., Yan, H., Li, H., Jiang, Z., Kan, X., Yang, H., Li, A., Cheng, R., 2011b. Removal of methylene blue from aqueous solutions by straw based adsorbent in a fixed-bed column. Chem. Engg. J. 173, 429–436.

Zhong, Z.-Y., Yang, Q., Li, X.-M., Luo, K., Liu, Y., Zeng, G.-M., 2012. Preparation of peanut hull-based activated carbon by microwave-induced phosphoric acid activation and its application in remazol brilliant blue R adsorption. Ind. Crops Prod. 37, 178–185.